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Electron Beam Radiation Damage and High-resolution Electron Microscopy of Poly(aryl-ether-ketone) Crystal

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Possibility of obtaining high-resolution images of poly(aryl-ether-ketone) [PEK] crystal was discussed on the basis of its measured total end-point dose [TEPD], i.e., the electron dose needed to lose all crystalline reflections in the electron diffraction pattern of the crystal. The TEPD value of PEK crystal, which was estimated at 0.21 C/cm² for 200 kV electrons, suggested that PEK is tough against electron irradiation enough to take its high-resolution images with a transmission electron microscope. Really, high-resolution images of PEK crystals were successfully obtained.

KEY WORDS: Poly(aryl-ether-ketone)/ Electron irradiation damage/ High-resolution electron microscopy/ Polymer crystal

INTRODUCTION

Poly(aryl-ether-ketone) [PEK] is a kind of rigid polymer with excellent properties such as high thermal stability and chemical resistance, and its repeating unit is -C₆H₄OC₆H₄CO- with all *para* linkages of phenylene rings. PEK has a melting temperature of about 350°C and a glass-transition temperature of about 155°C. The crystal structure of this polymer determined by X-ray diffraction was reported by Hay *et al.*,¹⁾ as being very similar to those of poly(aryl-ether-ether-ketone) [PEEK], poly(*p*-phenylene oxide) [PPO] and poly(*p*-phenylene sulfide) [PPS]^{2,3)}: the PEK chains have an extended conformation in which the phenylene rings deviate alternatively clockwise and anti-clockwise at an angle of 34° ± 0.6° from the plane of the zigzag backbone. Unit cell dimensions for PEK were *a* = 0.765 nm, *b* = 0.597 nm and *c*(chain axis) = 1.009 nm, and the space group was Pbcn (orthorhombic).

A high-resolution transmission electron microscope [HREM] is a powerful tool to study the microstructure of solid state by direct imaging. It was, thus, widely used in structural studies of metals and semi-conductors owing to their durability against electron irradiation. As for polymer crystals, it was difficult to apply this method to them because of their sensitivity to electron beam radiation.⁴⁾ Though electron microscopy was, therefore, used normally in the morphological study of polymer solids for many years,⁵⁻¹⁰⁾ recently HREM has started to be applied to the studies of polymer crystals.¹¹⁻¹⁵⁾

In this article we examine the stability of PEK crystal against electron irradiation and discuss the possibility of obtaining its HREM images.

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EXPERIMENTAL

1. Sample Preparation

a) Crystalline thin films with spherulitic structure

PEK, a research sample, was dissolved in α -chloronaphthalene in a concentration of 1 wt%.^{7,18)} The resulting solution was cast on freshly cleaved mica at about 250°C to yield thin films for transmission electron microscopy [TEM], and then the films on mica were dried overnight in a vacuum oven at about 180°C. The films thus prepared were melted on a hot plate at 350 – 370°C for 30 sec and then rapidly transferred for crystallization to another hot plate whose temperature was in the range of 220 – 300°C. After crystallization for the desired periods of time, the samples were quenched in air, removed from their substrate (mica) by flotation in distilled water, and finally deposited onto Au-coated microgrids for morphological and electron diffraction investigations. Figure 1a shows a TEM photograph of a PEK spherulite.

b) As-polymerized samples

Before the activation of polymerization was completed, thin pieces of freshly cleaved

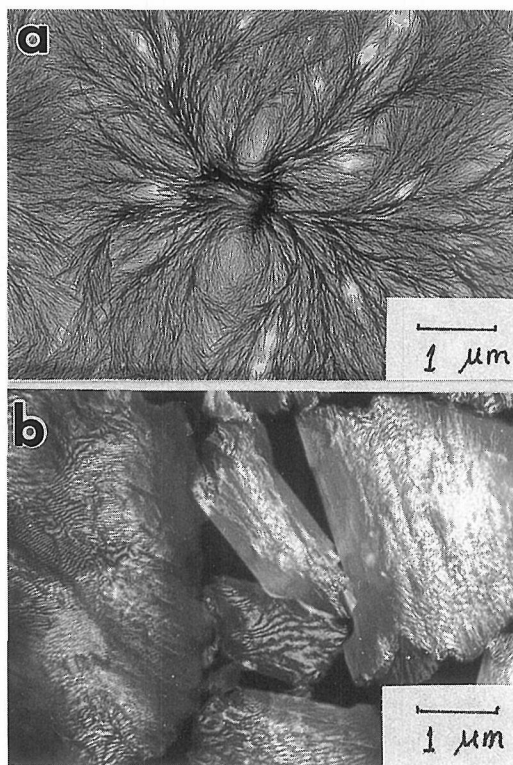


Fig. 1 TEM photographs of PET specimens.
(a) Crystallized from an α -chloronaphthalene solution on freshly cleaved mica at 250°C.
(b) As-polymerized/crystallized in the activation oven for about 2 hours.

mica were put in the activation oven for about 2 hours. The mica pieces were taken out of the oven, put into alcohol to remove excess polymers off from the surface of mica, and dried overnight in a vacuum oven. The PEK samples were detached from the mica in the water and deposited on microgrids. Figure 1b is a TEM photograph of as-polymerized PEK crystals, which was taken in the dark-field mode.

2. HREM Observation

A JEOL JEM-2000EX high-resolution transmission electron microscope with a side entry goniometer was used in this work. It was operated at 200 kV. The high-resolution pole piece (SHP) used here has a spherical aberration coefficient [Cs] of 1.9 mm. A condenser aperture of 100 μm was employed and the spot size "3" was selected. A minimum dose system [MDS] was used in the image-recording process in order to minimize the radiation damage. The size of objective aperture corresponds to 4 nm^{-1} . The HREM images were recorded on Kodak SO-163 photographic plates at direct magnifications ranging from 100,000 to 200,000. The range of electron dosage on the specimen for image recording was from 0.02 C/cm^2 to 0.2 C/cm^2 . Electron beam current was measured with a current meter connected to the Faraday cup inserted in the microscope.

RESULTS AND DISCUSSION

1. Radiation Damage of PEK Crystals

Generally speaking, electron beam radiation affects some of physical properties of the specimen through mass loss and cross-linking. In this study, the loss of crystallinity was used to quantify the radiation damage of PEK crystals. The total end-point dose (TEPD: the electron irradiation dose which is needed for a given crystal to lose all its crystalline reflections in the diffraction pattern) was used to know the feasibility of obtaining high-resolution images of the crystal. The relationship between TEPD and the expected line-resolution limit d [nm] of lattice fringes which are directly observable in the electron micrographs is described with the modified Rose equation²⁰⁾

$$d = 1.5/C(62420 \cdot fQ)^{1/2}, \quad (1)$$

where C and f are the contrast and the net utilization factor, respectively. Empirically, $C = 0.1$ and $f = 0.25$ have been used.^{16,17)} The quantity Q is the total end-point dose of the specimen in units of Coulomb/ cm^2 [C/cm^2].

Figure 2 shows a series of selected-area electron diffraction patterns corresponding to $\langle 001 \rangle$ incidence of electron beams onto the PEK crystal at different radiation doses. The reflections recognized in these patterns are all spot-like. This feature is different from those observed in PEEK¹⁴⁾ and PPS,²⁴⁾ both of which showed arced reflections. The spot-like reflections indicate that the PEK crystal has good coherency over a fairly wide specimen-area corresponding to the size of selected-area aperture used in this experiment. As demonstrated in Fig. 2, the intensity of the crystalline reflections decreased with increasing radiation dose, and finally the reflections disappeared. The 110 reflection was the most stable, and the TEPD was, thus, estimated at 0.21 C/cm^2 . This TEPD value is about twice that of PEEK¹⁴⁾ and is comparable to that of PPS,²¹⁾ in both of which high-resolution im-

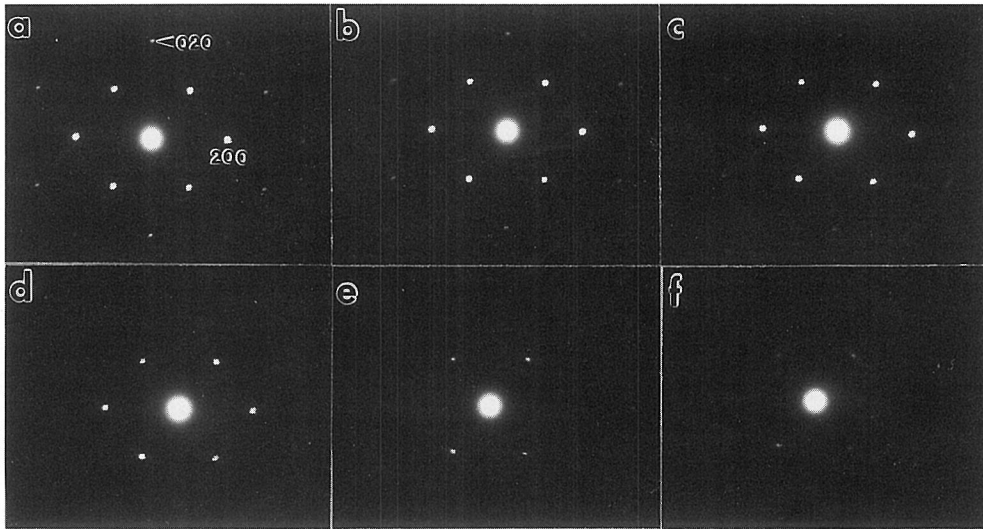


Fig. 2 A series of selected-area electron diffraction patterns of PEK crystal corresponding to the $\langle 001 \rangle$ incidence of electron beams.

The patterns were recorded at an irradiation dose of

- (a) 0.000 C/cm^2 ; (b) 0.020 C/cm^2 ;
 (c) 0.075 C/cm^2 ; (d) 0.100 C/cm^2 ;
 (e) 0.175 C/cm^2 ; (f) 0.200 C/cm^2 .

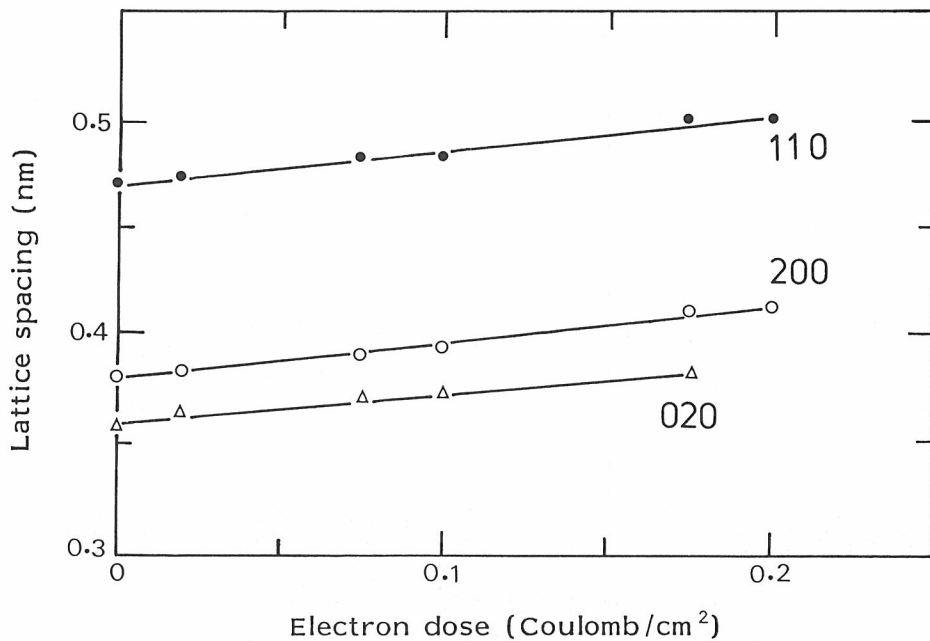


Fig. 3 Dependence of (110), (200) and (020) lattice spacings of PEK crystal on electron irradiation doses.

ages were already obtained. According to the equation (1), the expected line-resolution limit for PEK was calculated as 0.26 nm. This value is smaller than the lattice spacings of 110 and 200 reflections, which spacings are 0.471 nm and 0.385 nm, respectively. So it is possible to obtain lattice images of PEK crystals at room temperature. Another feature of Fig. 2 is the gradual, almost linear increase in lattice spacing for all of the 110, 200 and 020 reflections with increasing radiation dose (see Fig. 3), though the slope of the line for 200 is slightly steeper than those for the others. This feature reveals that the PEK crystal lattice expands in the *a*-axis direction and also in the *b*-axis direction with increasing radiation dose.

The intensity, $I(D)$, of a particular reflection at a dose, D , is given by the following equation⁴⁾

$$I(D) = I_0 \cdot \exp(-D/D^*) + I_\infty, \quad (2)$$

where I_0 and D^* are, respectively, the intensity of the reflection at zero dose and the "characteristic dose" at which the intensity is reduced by a factor of $1/e$. Here, I_∞ is defined as the intensity at infinite doses, or at a dose at which no further change in intensity is observed. It corresponds to the background level in the microdensitometer trace of the reflection in question in the electron diffraction negatives recorded at high doses. The characteristic doses for 110 and 200 reflections were estimated at 0.17 C/cm² and 0.15 C/cm², respectively. The 110 and 200 lattice spacings increased by 4.7% and 7.4% of their starting values at respective characteristic doses. Kumar *et al.*⁴⁾ have shown that the stability of a polymer structure against the electron beams is strongly dependent on its thermal stability/melting temperature. The characteristic doses for PEK measured in this study are fairly higher than that expected from that correlation proposed by Kumar *et al.*⁴⁾, even if the difference in the accelerating voltage is taken into consideration. Since a similar situation has also been estimated for PPS by them, the tendency that the observed characteristic dose D^* is larger than the expected one seems to be common for the polymers with the similar crystal structure to that of PEK, but as they reported, the PEEK crystal was one of the polymer crystals exhibiting the good correlation.

2. High-resolution Image of PEK Crystal

PEK is composed of carbon, hydrogen and oxygen atoms. The contrast in its HREM image can be interpreted by the weak-phase-object approximation in a certain range of thickness.¹⁹⁾ Figure 4 is one of the high-resolution images of a PEK crystal, which correspond to the $\langle 001 \rangle$ incidence of electron beams, i.e., the incident electron direction parallel to the molecular axis in the crystal. Figure 5 is a computer-simulated image for an amount of underfocus of 106 nm corresponding to Fig. 4: the image simulation was carried out based on the reported crystal structure of PEK (see Fig. 6) using a program which was made for a personal computer by modifying the program²³⁾ developed by Ishizuka and Uyeda²²⁾ for multi-slice dynamical calculation. The simulated image illustrates that a dark spot in the high-resolution micrograph (Fig. 4) corresponds to a molecular chain of PEK viewed along the chain axis. A resemblance in image contrast between observed and simulated images confirms the validity of the structure of PEK crystal reported by Hay *et al.*¹⁾

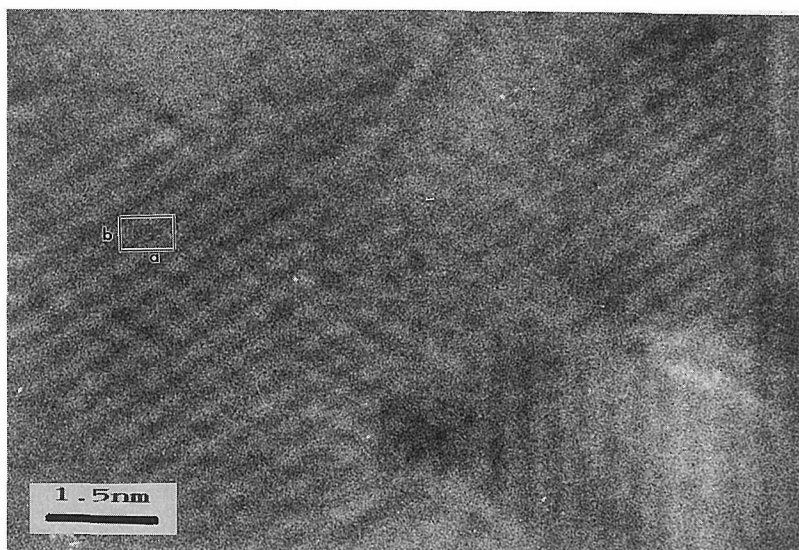


Fig. 4 HREM image of a PEK crystal viewed along the $\langle 001 \rangle$ direction.
The size of the objective aperture used to take this image corresponds to 4 nm^{-1} .

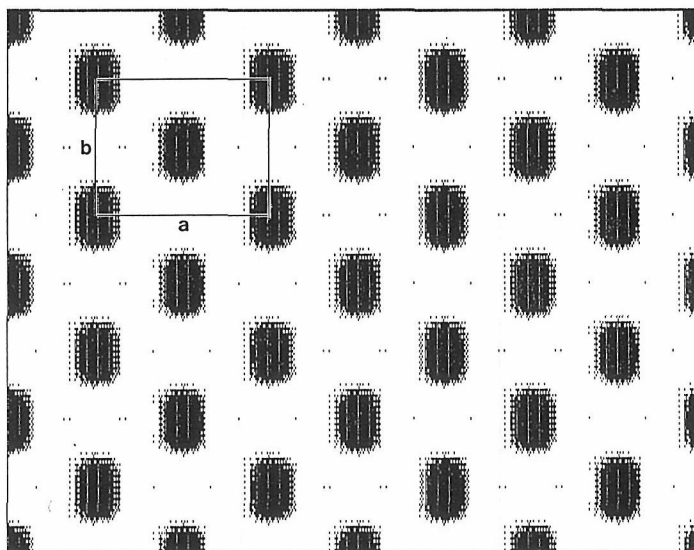


Fig. 5 Computer-simulated image of PEK crystal at an amount of underfocus of 106 nm based on the crystal structure model of Fig. 6, by using multi-slice dynamical calculation.^{22,23)} Slice thickness was equal to the c -dimension, and the slice number was 15. 121 beams were used in dynamical calculation of diffraction. The envelope function 5 (usual 1-st order partial coherent envelopes) was used in the calculation.²³⁾ The size of objective aperture was 4 nm^{-1} .

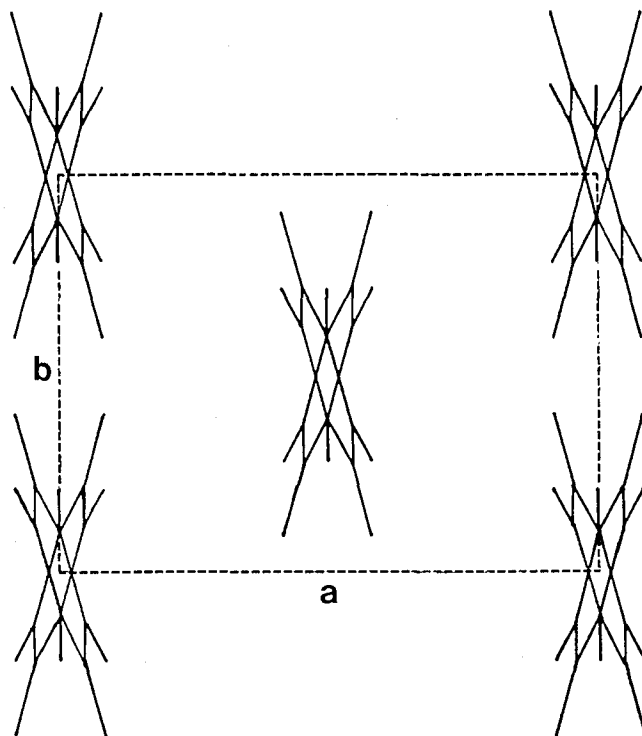


Fig. 6 Projection of the unit cell of PEK crystal onto the ab -plane along the c -axis (chain axis).
The space group of the crystal is $Pbcn$ (orthorhombic: $a = 0.765$ nm, $b = 0.597$ nm, $c = 1.009$ nm).¹⁾

insofar as its projection onto the plane perpendicular to the chain axis (c -axis).

Very recently, we have found a new crystal structure of PEK which seems to belong to the space group of $Pc2n$, and its projection onto the plane normal to the chain axis is predicted to be very similar to Fig. 6.¹⁹⁾ Accordingly, it might be difficult to distinguish between these two crystal structures of PEK in the HREM images corresponding to the beam incidence along their chain-axis. Discussion about the new crystal structure will be shown in the subsequent paper.¹⁹⁾

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